1 Introduction

On November 5, 1998, the Air Resources Board considered regulations that set emission standards for Low Emission Vehicles (LEV-II). Included in the regulations were tighter standards for emissions of nitrogen oxides (NO_X). During the LEV-II hearing, several witnesses suggested that lower NO_X emissions would be counter-productive for reducing ozone concentrations. As justification, these witnesses cited a phenomenon known as the "ozone weekend effect."

The "ozone weekend effect " refers to the interesting observation that ozone measurements in some locations are typically higher on weekends compared to weekdays. Examples of the ozone weekend effect can be seen in Figure 1-1. The effect occurs when the solid line is above the dotted line in each graph.

The ozone weekend effect is somewhat surprising because smog-forming emissions mostly come from sources, such as cars, trucks, and factories, that could be expected to produce a lower total of smog-forming emissions on weekends compared to weekdays.

After evaluating all of the testimony at the LEV-II hearing, the Board adopted the proposed regulations and directed the CARB staff to investigate the ozone weekend effect. The purpose of the study was to determine why the ozone weekend effect occurs and whether it demonstrates that NO_X reductions in California are counter-productive for reducing ozone.

In response to the Board's directive, the staff identified analyses using presently available data to investigate the ozone weekend effect. The analyses focused primarily on the South Coast Air Basin of California because of its rich stores of data from routine monitoring and special field studies. This report summarizes the results of the staff's work and recommends further research to address unresolved issues.

Objectives of this report

Previous studies of the ozone weekend effect have established that the ozone weekend effect is real but have not determined its cause(s). Some investigators have speculated concerning the cause(s) of the ozone weekend effect, but definitive answers were beyond the scope of their work.

The objectives of this report are to examine the ozone weekend effect and 1) determine its magnitude, 2) investigate hypotheses of potential factors contributing to it, 3) identify, if possible, its causes, and 4) evaluate its implications concerning ozone control strategies. These objectives are challenging; data may be sufficient for some objectives but insufficient for others. In addition, the implications may not be straightforward because the context and the results of intermittent <u>weekend</u> emission reductions may be quite different from the context and results of consistent <u>regulatory</u> emission reductions.

Background

Ozone formation

Essentially no ozone is directly emitted by pollution sources. Rather, it is formed in the atmosphere through a complex set of chemical reactions initiated by ultraviolet sunlight. The chemical reactions chiefly involve volatile organic compounds (VOCs) and NO_X ($NO + NO_2$).

Without VOCs and NO_X from human activities, ozone concentrations near the surface of the earth would be limited to approximately 15-20 parts per billion (ppb). With industrialization, the background tropospheric ozone concentration has increased to 20-25 ppb (Volz and Kley, 1988). In areas downwind of metropolises, regional background ozone concentrations can be 40 ppb or more. These increases in ozone increase the oxidation capacity of the atmosphere and impact essentially every reactive trace gas. Furthermore, the ozone increase impacts radiation budgets since ozone not only absorbs ultraviolet radiation but is also a greenhouse gas and therefore a concern from a global climate change perspective.

When anthropogenic VOCs and NO_X are present, ozone concentrations can reach levels that compromise human health. Federal and state standards for ozone indicate that concentrations as low as 90 to 120 ppb for one hour or more can adversely affect lung function. If exposure to ozone lasts 8-hours or longer, concentrations as low as 80 ppb can have an adverse impact. As illustrated in Figure 1-2, ambient air quality standards (see CAAQS) are frequently exceeded in the South Coast Air Basin.

Ambient ozone (O_3) is formed from the reaction of free oxygen atoms with molecular oxygen (O_2). The main source of free oxygen atoms in the lower atmosphere (troposphere) is photolysis of nitrogen dioxide (NO_2), a constituent of NO_X. In this photochemical reaction, NO_2 absorbs ultraviolet sunlight and dissociates into NO and a free oxygen atom (O) which combines with the abundant oxygen molecule (18% of Earth's atmosphere) to form O_3. Ultraviolet solar radiation, NO_X, and VOCs are needed to drive the complex ozone-forming processes. VOCs react in the atmosphere to form radicals, which convert NO to NO_2 without the destruction of an O_3 molecule. Photolysis of the NO_2 then leads to additional ozone formation.

The importance of NO_2 photolysis on a global scale is illustrated by an interesting observation. When VOCs are weighted by their ozone-forming potential (reactivity), ozone concentrations in very different environments are strongly correlated with NO_X concentrations but only slightly correlated with VOC concentrations (Seinfeld & Pandis, 1998; Chameides, 1992; National Research Council, 1991).

The relationship between ozone, NO_X, and VOCs is complex. For example, NO_X promotes ozone formation when VOCs are relatively abundant but restricts ozone formation when VOCs are relatively scarce. The sensitivity of ozone to VOC and NO_X levels can vary depending on the time of day (Tonnesen and Dennis, 2000a). In a simplification dependent on VOC reactivity, when VOC/NO_X are ratios greater than 8 to 10 ppbC/ppb, NO_X tends to promote ozone formation, but when the VOC/NO_X ratio is less than 8 to 10 ppbC/ppb, NO_X tends to inhibit ozone formation. The VOC/NO_X ratio, in turn, can differ by location and time-of-day within a geographic area (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000).

The effect of the VOC/NO_X ratio may not be constant, however. Experiments in the 1990s indicate that the “reactivity” of VOCs decreases as NO_X decreases. Therefore, an increase in the VOC/NO_X ratio when emissions are high may lead to a greater proportional increase in ozone compared to the same increase in the VOC/NO_X ratio when emissions are lower (Carter, 1995).

The ozone weekend effect

The ozone weekend effect is not new. For the last 30 to 40 years, atmospheric scientists have noted that ozone concentrations can be somewhat higher on weekends than on weekdays at some locations (Levitt and Chock, 1976; Elkus and Wilson, 1977). This is interesting because concentrations of ozone precursors seem to decrease on weekends almost everywhere. Atmospheric scientists coined the term "weekend effect" to describe the phenomenon.

Before the 1990s, analyses of the ozone by day of week effect seldom found statistically significant differences, although patterns were consistent from study to study. Quantitative estimates of the differences were highly uncertain. In the 1990s, however, studies used additional data and improved analytical methods to show the ozone weekend effect is “real.” One recent study provided quantitative estimates of the ozone weekend effect in three regions of California – the South Coast Air Basin, the San Francisco Bay Area Air Basin, and the Sacramento Metropolitan Area (Austin and Tran, 1999).

A large body of weekday-weekend studies has revealed the following facts about the ozone weekend effect:

- It is slightly greater for 8-hour average ozone than for 1-hour average ozone.
- It occurs in many parts of the world (Bonnimann and Neu, 1997; Pont and Fontan, 2001; Borrell, 2003).
- It is most commonly associated with urban rather than rural locations.
- It can change over time (e.g., from Saturday to Sunday, spatial extent).
- It may persist despite downward trends in ozone on all days of the week.
- It is different from the weekend effect exhibited by other major pollutants.

Ozone control strategies in California

The Air Resources Board is charged with protecting the public health and welfare from the adverse effects of air pollution. To reduce health risks due to ozone and some other pollutants, the ARB has followed a policy for more than 20 years of reducing emissions of both VOCs and NO_X. Additional benefits of this policy include reductions in nitrogen dioxide, particulate nitrates, acid deposition, and certain toxic air contaminants. Reductions in these ambient pollutants tend to improve visibility and represent significant health benefits.

From the mid-1970s into the 21st century, the ozone control strategy implemented in the SoCAB included reductions of both VOC emissions and NO_X emissions. Early NO_X reductions were achieved by statewide controls on emissions from motor vehicles combined with local controls on emissions from industrial sources, such as power plants and cement kilns.

The policy of reducing VOCs and NO_X concurrently has been pursued most vigorously in the South Coast Air Basin, where it has been dramatically successful. As seen in Figure 1-2, the frequencies of unhealthful ozone concentrations have declined steadily in the past 35 years. In 1970, Stage II episodes (350 ppb or more) occurred on 70 days per year but were completely eliminated by 1989. Stage I episodes (200 ppb or more) occurred on 180 days per year but are now quite rare. Even exceedances of California's protective state standard (90 ppb) have been reduced more than 60 percent.

Other measures of ozone air quality confirm the record of success for combined reductions of VOCs and NO_X.

Figure 1-3 tracks the changes in "peak" ozone concentrations for the past 35 years. Peak concentrations have been reduced approximately 70 percent during this period. Though more remains to be done to achieve national and state standards, the success of concurrent VOC and NO_X reductions is very impressive. [Note: Ozone data from the 1960's and early 1970's were adjusted to their equivalent values when using present day (UV-absorption) measurement methods.]

Ambient air quality status and trends

During the late 1960s and much of the 1970s, the highest ozone concentrations (Stage II and Stage III episodes) in the SoCAB occurred most frequently on Thursdays and Fridays with Sunday having the fewest episodes (Figure 1-4 and CARB, 1978). A Stage II episode occurs when a 1-hour ozone concentration is 350 ppb or more. A Stage III episode occurs when a 1-hour ozone concentration is 500 ppb or more. It is interesting to note that none of the 14 Stage III episodes between 1964 and 1977 occurred on a weekend (Figure 1-4). Nevertheless, some sites, primarily in the western portion of the basin where ozone concentrations are relatively low, typically had higher ozone concentrations on Sundays than on weekdays.

While ozone concentrations declined generally in the SoCAB, the rate of improvement on weekends was somewhat slower than the rate of improvement on weekdays. Over the years, typical weekday concentrations of ozone became smaller than typical weekend concentrations. By the late 1990s, Sunday became the day with the most ozone episodes instead of the fewest. The term "ozone weekend effect" was coined to describe this tendency for ozone concentrations to be greater on weekends than on weekdays. This phenomenon coincides with presumably lower emissions of VOCs and NO_X on weekends compared to weekdays. Ambient data indicate that the concentrations of carbon monoxide (CO) and NO_X on weekends decline proportionally more than VOCs.

Between 1987 and 1997, ozone concentrations declined for all days of the week at all locations in the SoCAB. Less progress has occurred in the San Francisco Bay Area, the Sacramento Valley, and the San Joaquin Valley. VOC control plans are in place in these air basins. However, the SoCAB NO_X control efforts are more aggressive than in the other air basins which rely heavily on statewide controls on motor vehicles. The SoCAB efforts have been enhanced to also reduce secondary PM formation while the SFBAAB has reduced NO_X to ameliorate the impacts of ozone transport to downwind air basins. From 1987 to 1997, peak ozone concentrations declined on average by 33 percent in the SoCAB but only 9 percent in the SFBAAB, 10 percent in the Sacramento Valley, and 5 percent in the San Joaquin Valley (Austin & Tran, 1999). Although the SoCAB may also have the most aggressive VOC controls, the NO_X reductions may be an important factor in the greatly improved ozone air quality in the SoCAB. This is illustrated in Figure 1-5, which shows the trend of ambient NO_X concentrations. Comparison with the trends of ozone exceedances in Figure 1-2 (and even more so with the trend of NAAQS exceedances) indicates that the greatest improvement in ozone air quality occurred during the period of greatest NO_X reductions.

Analytical complexities and approaches to investigating the weekend effect

Data from regions with different meteorology, a different mix of emission sources, and different control programs may help elucidate the ozone weekend effect. For example, in clean environments, unaffected by anthropogenic emissions, one would expect no difference between ozone concentrations on weekdays and weekends. In NO_X-limited areas, one might expect the lower NO_X on weekends to result in lower ozone concentrations on weekends. In VOC-limited areas, one might expect the lower NO_X on weekends to result in higher ozone concentrations on weekends.

However, the behavior of ozone in air basins may differ significantly from the behavior of ozone in most smog chamber experiments or air quality models. In an air basin, initial conditions, boundary conditions, wind fields, clouds, mixing heights, carryover, and hourly input of fresh emissions may all differ significantly from day to day. Such differences are very difficult to simulate using smog chambers. Although photochemical simulation models include these and other details, they do so imperfectly. Furthermore, it may not be feasible to validate these models for suitable sequences of weekday and weekend conditions.

Assuming meteorology is unaffected by the day of the week, the fact that patterns of human activity are different on different days of the week is the only reasonable explanation for the ozone weekend effect. Anthropogenic pollutants are emitted at different times and locations on different days of the week. These emissions interact with meteorology (e.g., dispersion, dilution, and deposition) to generate ozone and particulate matter through a complex set of photochemical reactions. To identify the cause(s) of the ozone weekend effect, the temporal and spatial patterns of emission activity, the overall emission inventory, meteorology, and photochemistry will need to be woven together.

Seven hypothetical causes of the ozone weekend effect are identified in Chapter 2 of this report. The hypotheses, which are not mutually exclusive, are the following:

- NO_X reduction
- NO_X timing
- Carryover near ground-level
- Carryover aloft
- Increased weekend emissions
- Aerosols and UV radiation
- Ozone quenching

The results of various analyses of ambient air quality and activity data are used to characterize day-of-week patterns and to evaluate for consistency with the hypotheses. Each of these hypotheses includes multiple disciplines that need to be integrated and corroborated in the process of isolating the factors contributing to the ozone weekend effect.

The long-term and extensive monitoring network of the SoCAB, its relatively high pollutant concentrations, and its large population make this area most useful for analyzing the ozone weekend effect. Most of the analyses in this report focus on the South Coast Air Basin. Figure 1-6 shows the locations of air basins in California and highlights the SoCAB. A map displaying topographic features and county boundaries of the SoCAB is provided in Figure 1-7. Maps portraying the air quality monitoring network in the SoCAB is presented in Figure 1-8 and Figure 1-8a. The core set of monitoring sites that will be referred to in many chapters is listed in the caption. A map portraying the transportation network of freeways and highways in the SoCAB is presented in Figure 1-9.

This report examines air quality and activity data rather than emission inventories. Efforts are being undertaken to better determine how emissions actually differ between weekdays and weekends. Inventories of weekend emissions are still being developed and the eventual goal is to have day-of-week inventories. Nevertheless, Table 1-1 is provided to indicate the relative strength of major types of emission sources in the SoCAB on an annual basis over the years. Note that mobile sources dominate the emissions of VOCs (labeled ROG in the table), NO_X, and CO. Also note that the contribution of diesel vehicles is has become increasingly significant for NO_X but has always been minor for VOCs and CO. Also noteworthy is the relative emphasis on the control of precursors. During the 1980s, the control efforts primarily reduced VOCs; during the 1990s, both precursors were reduced significantly with a greater emphasis on VOC. During the first decade of the 21st century, the precursors are anticipated to decline significantly again but equally. Carbon monoxide (CO), a minor precursor of O_3 and a criteria pollutant itself, has also declined significantly and in proportion with the VOC reductions.

Furthermore, VOC control efforts through fuel reformulation have included substantial reductions of toxic air contaminants such as the human carcinogen, benzene.

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Table 1-1. Annual average emissions of ROG (aka VOC), NO_X, and CO (tons/day) by source category in the South Coast Air Basin, 1980, 1990, 2000, and 2010

	ROG				NO_X				CO			
Source Category	**1980**	**1990**	**2000**	**2010**	**1980**	**1990**	**2000**	**2010**	**1980**	**1990**	**2000**	**2010**
Stationary Sources	**420**	**404**	**186**	**159**	**361**	**182**	**98**	**74**	**289**	**101**	**52**	**58**
Area-Wide Sources	**231**	**227**	**200**	**168**	**36**	**30**	**32**	**29**	**178**	**230**	**308**	**352**
On-Road Mobile Sources:	**1396**	**900**	**470**	**227**	**945**	**1063**	**679**	**351**	**11721**	**9030**	**4631**	**2104**
Diesel	9	16	10	7	153	352	239	159	37	76	48	35
Gasoline	1386	883	460	220	791	711	440	192	11684	8954	4583	2069
Other Mobile Sources	**138**	**166**	**148**	**78**	**366**	**364**	**292**	**226**	**957**	**1110**	**893**	**781**
Natural Sources	**125**	**125**	**125**	**125**	**0**	**0**	**0**	**0**	**106**	**106**	**106**	**106**
Total	**2310**	**1821**	**1128**	**757**	**1708**	**1638**	**1101**	**680**	**13251**	**10578**	**5990**	**3401**
% Change (anthropogenic)		**-22%**	**-41%**	**-37%**		**-4%**	**-33%**	**-38%**		**-20%**	**-44%**	**-44%**

NOTES:
Data for anthropogenic sources are derived from The 2002 California Almanac of Emissions & Air Quality published by CARB.
Data for natural sources are from the following: ROG (Benjamin, et al., 1997, *Atmospheric Environment*, Vol. 31, pp 3087 - 3100); NO_X (negligible natural sources); CO (CEFS 1996 Base Year Forecast Scenarios for 2000 Almanac). No changes are expected in emission rates for natural sources between 1980 and 2010.

Figure 1-1. Ozone trends from 1980 through 1998 for weekdays and weekends at Azusa, LA - North Main St., and Lake Gregory in the South Coast Air Basin.
(Ozone trend statistic is the mean of the 2nd - 11th highest daily maximum 1-hour concentrations each year.

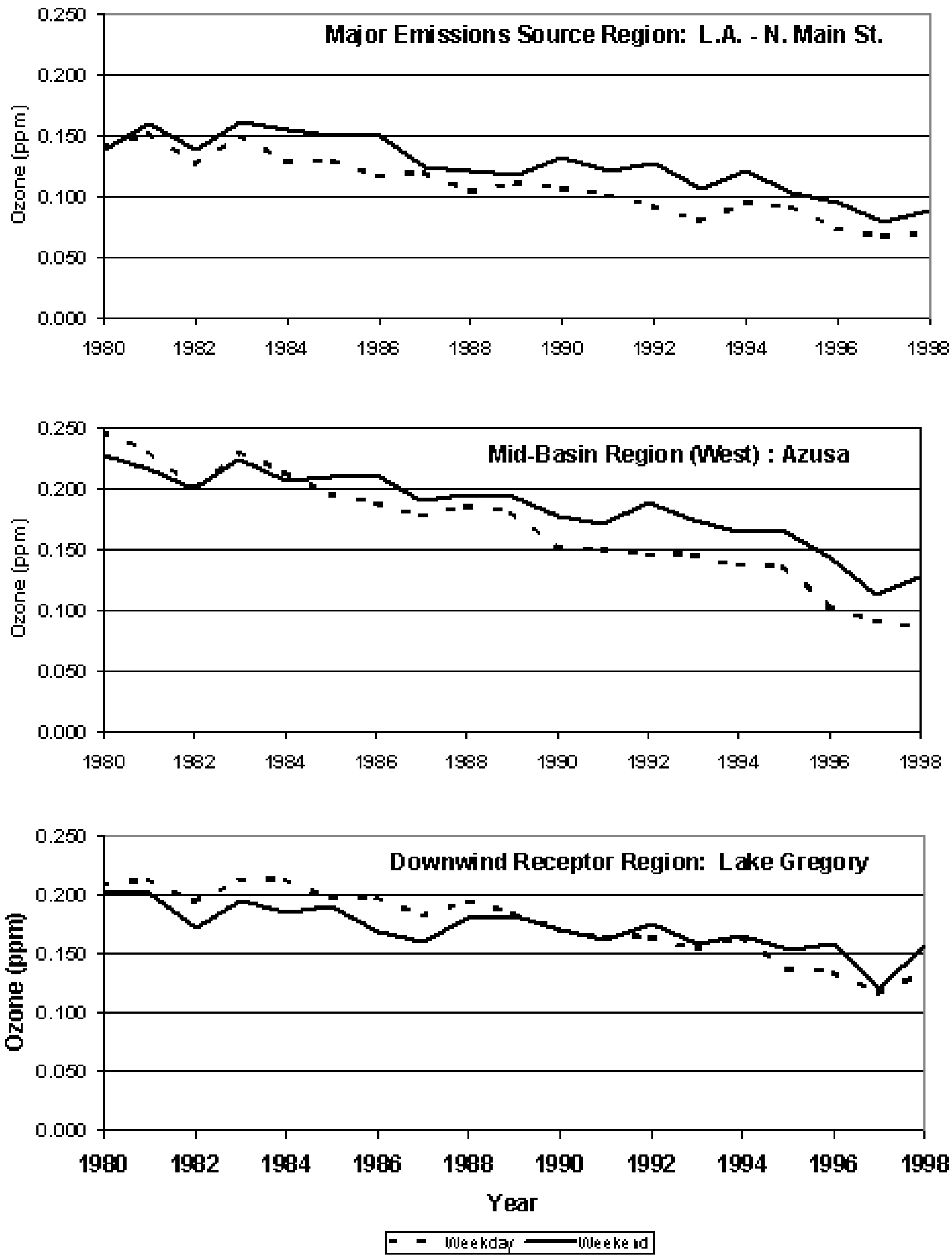


Figure 1-2. Number of days per year when the California Ambient Air Quality Standard for ozone was exceeded and when Stage I and Stage II ozone episodes occurred within the South Coast Air Basin, 1965 – 2000

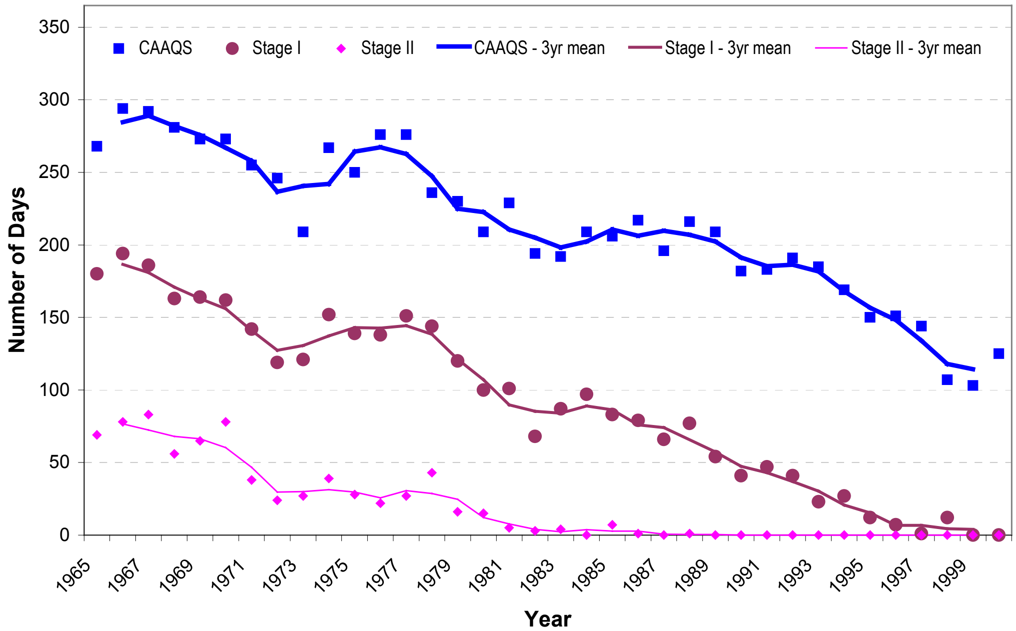


Figure 1-3. Trends of peak ozone levels (annual maximum 1-hour and mean of top 30 daily maximum 1-hour) observed in the South Coast Air Basin, 1965 – 2000

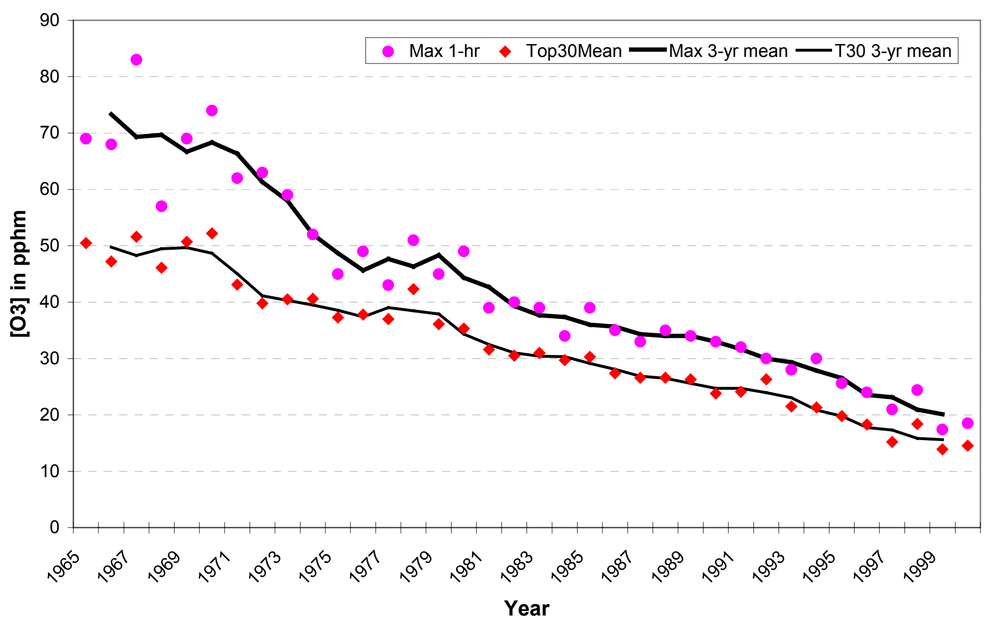
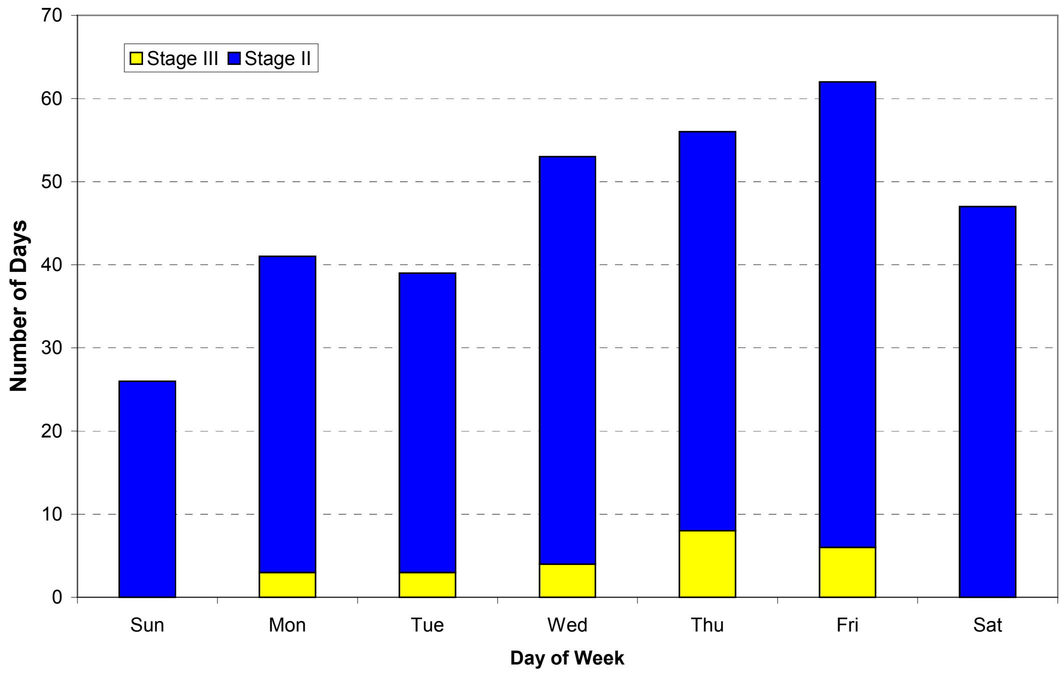


Figure 1-4. Frequency of Stage II* and Stage III** ozone episodes by day of the week in the South Coast Air Basin, 1964 - 1977.



* Stage II = 1-hour ozone level ≥ 0.200 ppm

** Stage III = 1-hour ozone level ≥ 0.350 ppm

Figure 1-5. Oxides of nitrogen air quality trend in the South Coast Air Basin, 1980 – 2000. Composite of daily average NO_X levels at 18 monitoring sites.

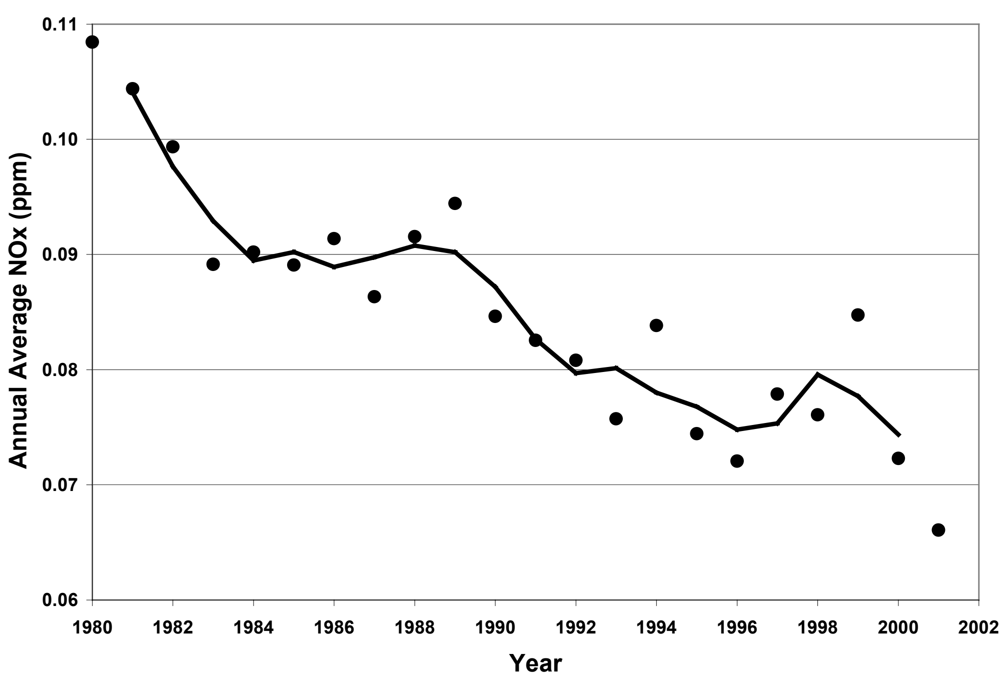


Figure 1-6. Outline of the State of California showing the boundaries of air basins. The South Coast Air Basin, the focus of most analyses in this report, is highlighted to show its location and size relative to the other 14 air basins in California.

Figure 1-7. Map showing the topography, counties, and major regions in and near the South Coast Air Basin.

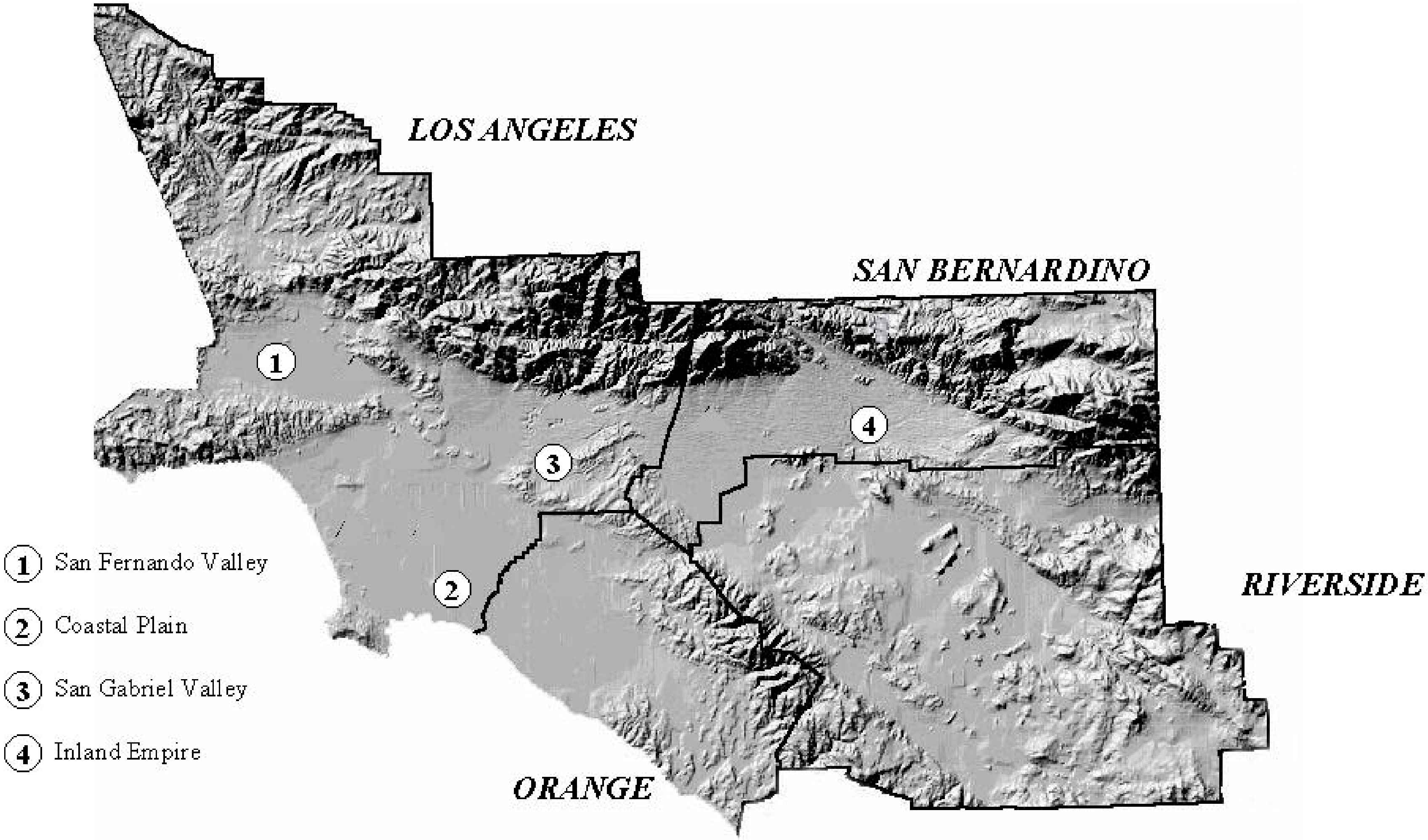


Figure 1-8. Map showing the location of the monitoring sites used in many of the analyses in this report. The "core" monitoring sites used include: Orange County – Anaheim; San Bernardino County – Lake Gregory and Upland; Riverside Coutny – Riverside-Rubidoux; Los Angeles County – Azusa, Burbank, Hawthorne, LA-N. Main, and Lynwood.

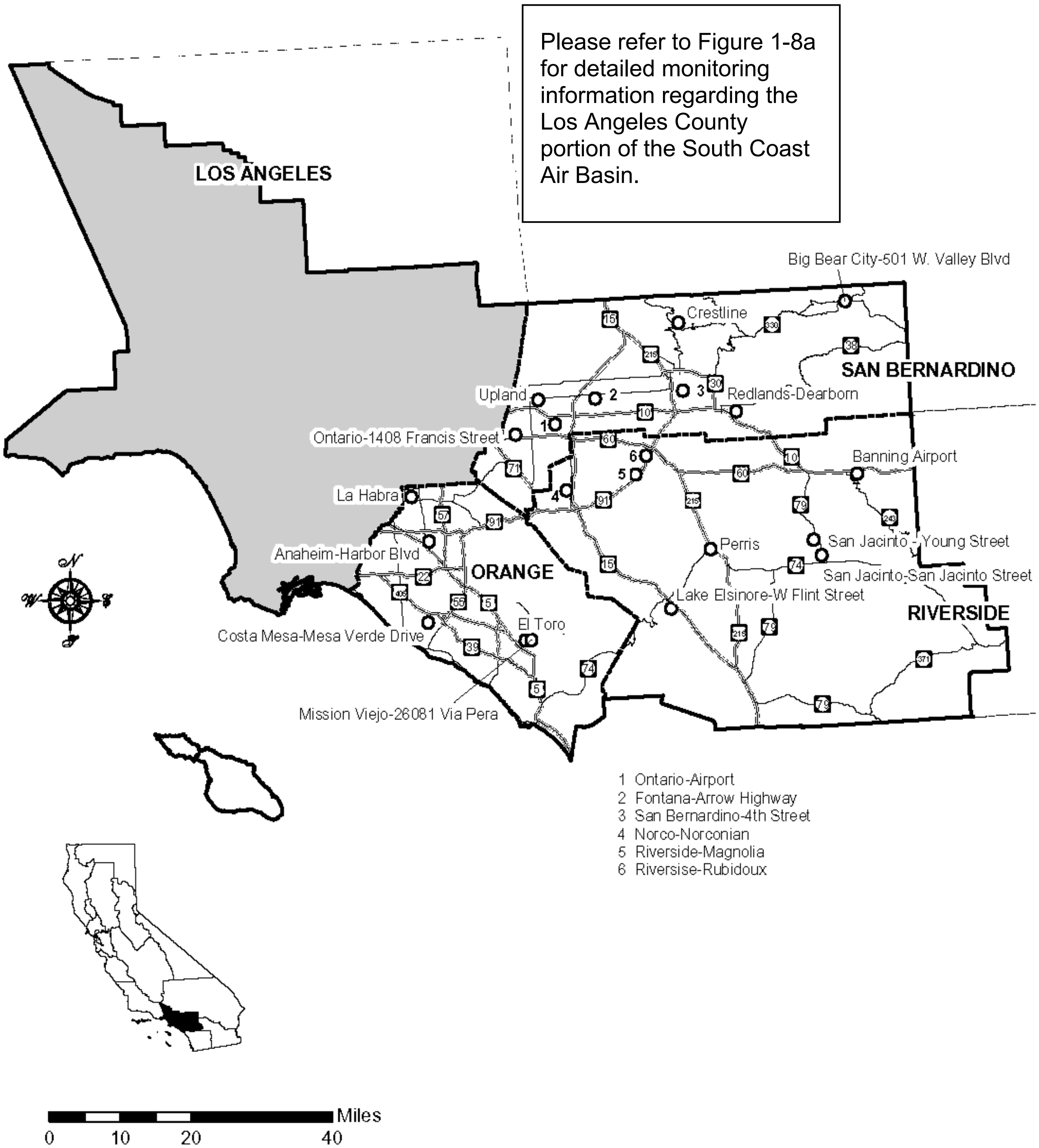


Figure 1-8a. Map showing the location of the monitoring sites in Los Angeles County.

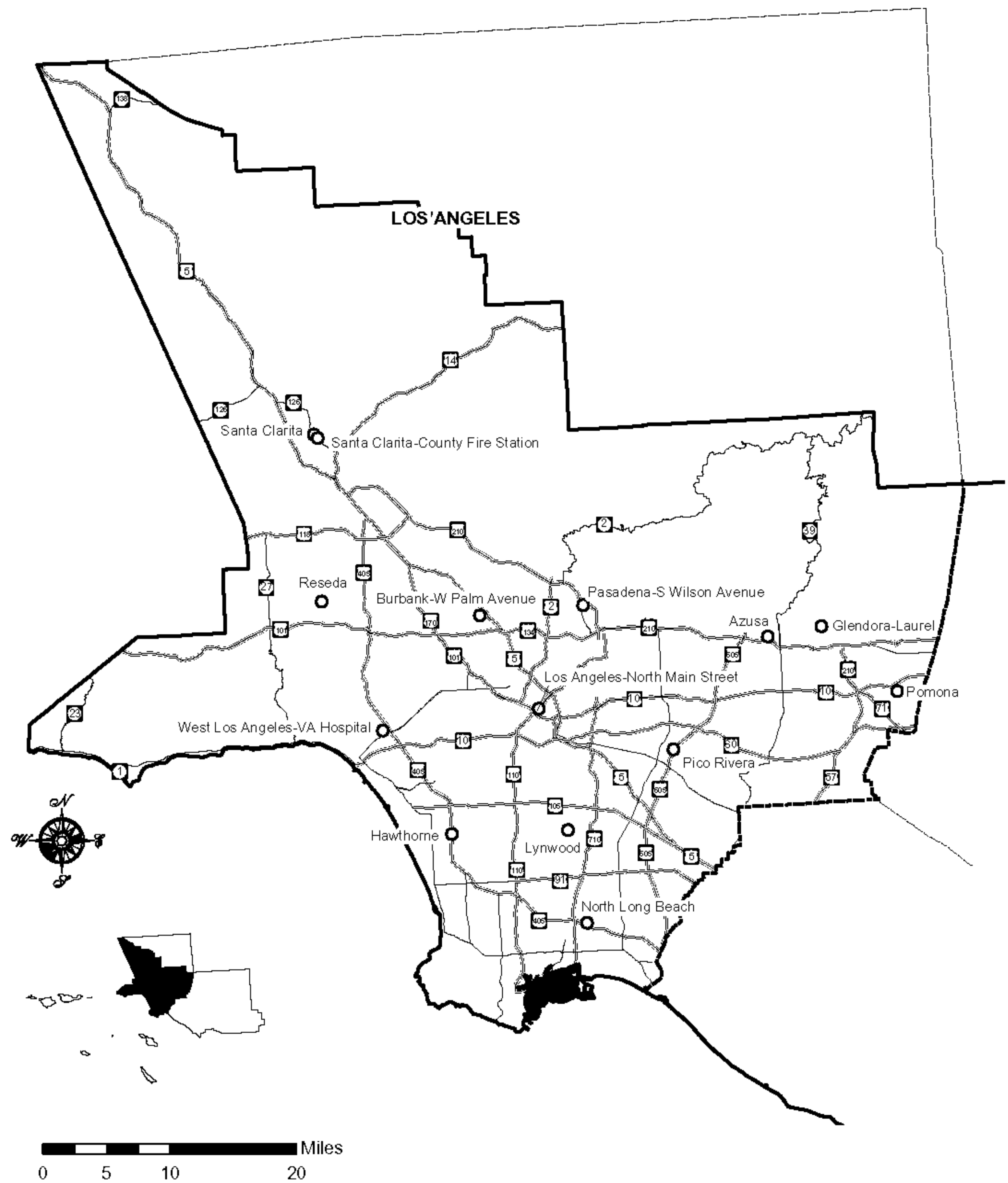


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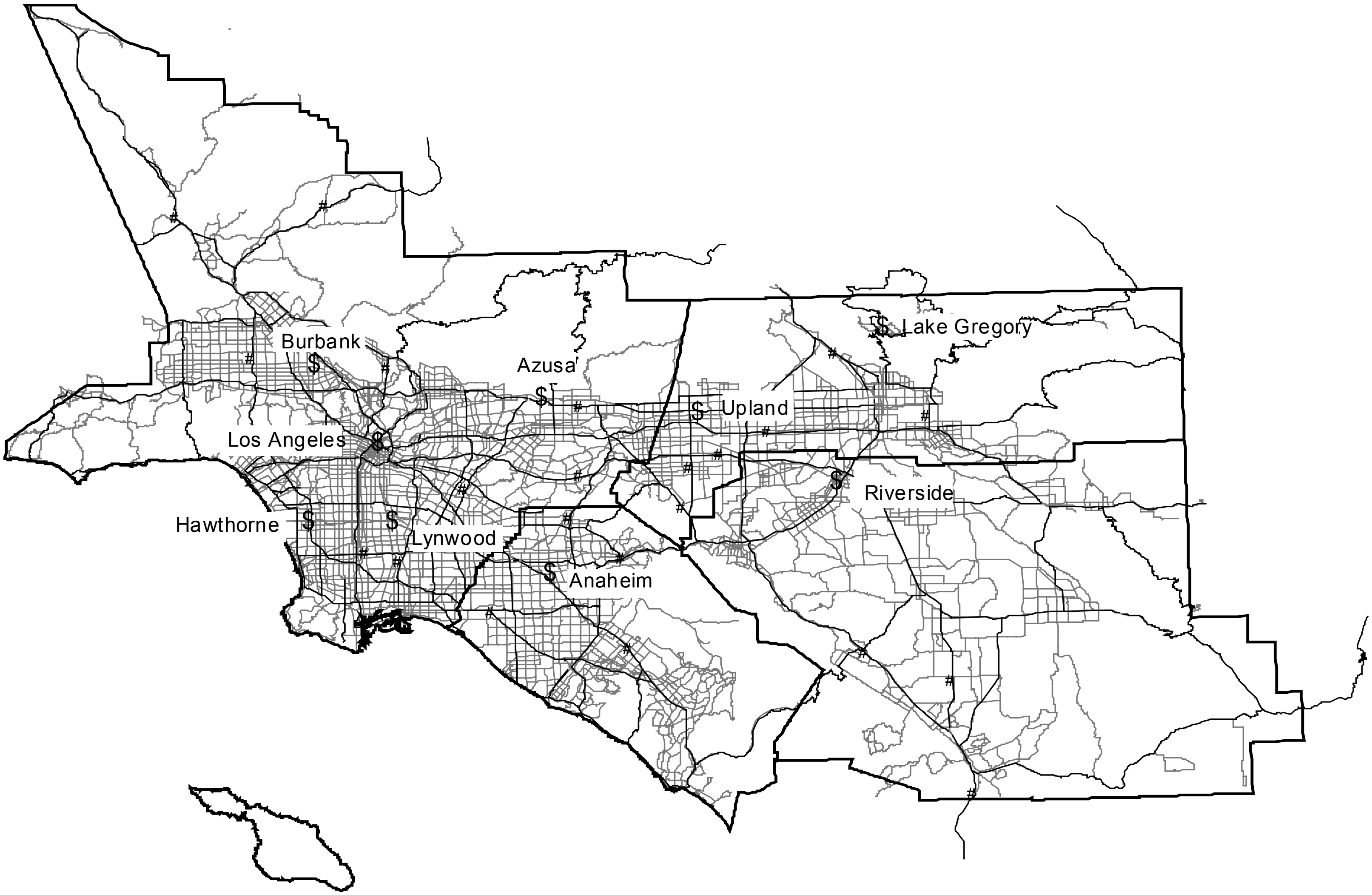
Figure 1-9. Map illustrates the greater roadway density in the western half of the South Coast Air Basin.



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